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Chemistry and Technology of the Cosmetics and Toiletries Industry

Second edition

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Preface to the first edition

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E. SPIESS

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l to operator safety). The product is diluted to form a rinse. This is followed 'rinse' effect. Complexes of acid dyes are used [114].

small portion of the hair colourants are permanent and semi-permanent colourants.

tried over the years [114], including *in situ* by coupling on the hair, and is based on groups such as mono- or di- with the hair and to which an A good effect is difficult to obtain. Other systems involving the use of waving lotions) to break bonds within the hair for hair dyes have been proposed, but are not realistic.

For dyes are based on basic dyestuffs, which have a natural affinity for the hair, or on dyes with nitro derivatives of aromatic amines. The most commonly used base and active level dyes provided that the active level which retards the dyeing process, is suitable with salt, therefore a blend of dyes with low salt levels is preferred. Dyestuffs may be enhanced by the use of considerable swelling of the hair shaft, which can even more, leading to greatly increased dye uptake. Ingredients include benzyl alcohol, butyl alcohol, and monopropylene or dipropylene glycol. In some patents, some quite recent, cover ingredients have been in use for at least 25 years. The dyeing process is aided by using the hydrogen-bond which tends to be more porous near the cuticle. The hair tends to be more porous when dyed. Dye uptake may occur. This is aided by using levelling agents; the inclusion of Oleth-20, often helps. Pohl [118] and low molecular weight dyestuff. Permanent hair colourants are shown in

be achieved by using a combination of dyes. In practice, dyes absorb on the

Table 2.34 Formulations for semi-permanent hair colourants

	Liquid	Cream	Shampoo	Shampoo
Metallised dyes	—	—	—	—
<i>o</i> -Nitro- <i>p</i> -phenylene diamine	—	—	—	} total < 2.5 } total < 2
<i>p</i> -Nitro- <i>o</i> -phenylene diamine	—	—	—	
Basic dyes	< 1.0	< 1.0	< 1.0	
Ammonium lauryl sulphate, 30%	—	—	—	10
Cetyl trimethyl ammonium chloride, 30%	3	4	2	—
Cocoamidopropyl betaine, 30%	—	—	15	—
Oleth-20	0.5	0.2	—	0.5
Coconut diethanolamide	—	—	2	—
Cetostearyl alcohol	—	3	—	—
Glyceryl stearate (and) PEG-100 stearate	—	3	—	—
Hydroxypropyl methylcellulose	0.8	—	0.5	0.5
Triethanolamine	to pH 8	to pH 8	to pH 8.5	0.4
Citric acid	—	—	—	0.3
Preservative	q.s.	q.s.	q.s.	q.s.
Perfume	q.s.	q.s.	q.s.	q.s.
Benzyl alcohol	3	—	—	2
PPG-2 butyl ether	—	—	—	2
Deionised water	to 100	to 100	—	to 100

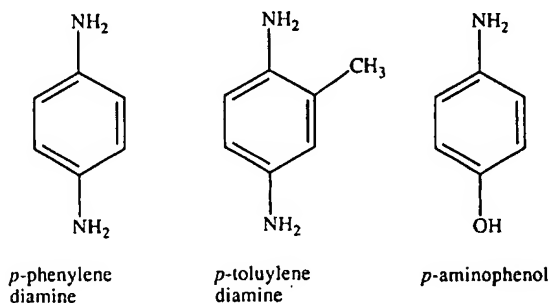
hair shaft at different rates, and are removed at different rates by shampooing. Consequently, products containing a mixture of dyestuffs can produce different colours when applied under different conditions (time, temperature, pH, etc.). In addition, the colour achieved may vary considerably from one type of hair to another, and after application and subsequent shampooing. Minimising these variations can be achieved by using colours that are close together; this approach is less likely to produce any unexpected (and usually unwanted) colours.

Basic dyes are more substantive from slightly alkaline bases, and metallised dyes from quite strongly acidic ones. Since salt can reduce substantivity, thickening, where required, is usually achieved by means of gums. Light-fastness is not usually a problem with semi-permanent colours (it can be with some of the temporaries) but scalp staining can occur, more so with solvent-assisted systems.

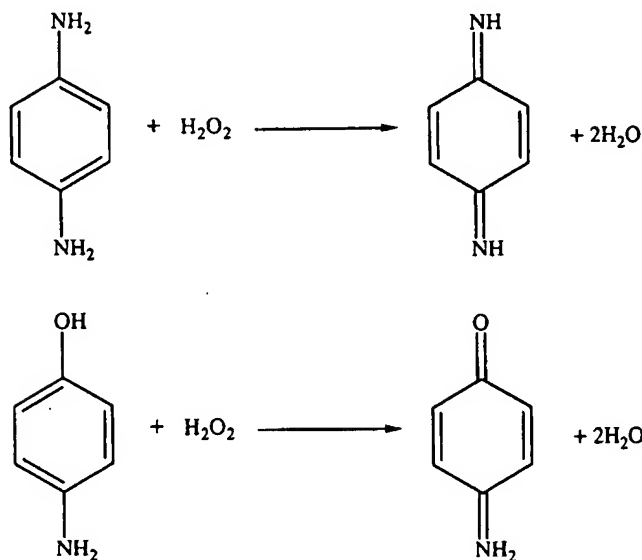
2.14.3 Permanent hair dyes

Permanent, or oxidation, dyes are fundamentally different to the other classes of dyestuffs that have already been considered. The dyes are formed during the dyeing process and are not present, as such, in the solutions before application. The products consist of two parts—a dye intermediate solution and an oxidising agent, the latter almost always being hydrogen peroxide. Dye intermediates are blends of primary intermediates and coupling agents, or modifiers, in a suitable base. During the permanent dyeing of hair the dye intermediate solution and the oxidising solution are mixed and applied

to the hair. The primary intermediates are gradually oxidised and then undergo coupling reactions with the modifiers. The primary intermediates are all small molecules that can, to a degree, penetrate the hair shaft, particularly under the wet, alkaline conditions prevailing during the dye application. The subsequent oxidation and coupling reactions produce much larger molecules, many of which are then 'trapped' within the hair shaft, thereby making the effect 'permanent'. The primary intermediate should be an aromatic compound with at least two electron-donating groups in the 1,2 or 1,4 positions. The most effective combinations are either two amino groups or one amino and one hydroxyl group, attached to a benzene or toluene ring. Other substituents may be present, either on the ring or *N*-substituted, and the ring itself may be non-benzene derived (e.g. pyridine). The most commonly used are:



Oxidation then takes place to form a quinonimine, e.g.



Coupling agents require the sul They are not easily directly ox with the quinonimines formed l

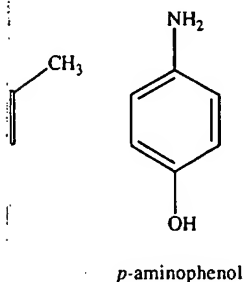
Coupling agents may be basec multiple ring systems, (fused or one stage of oxidative coupling large molecules [118]. The poss relatively few primary intermedi hair itself may modify or even ta theory that Bandrowski's basi with oxidation dyes is now wide hair shaft, oxidation and coupli outside the hair. The multitude to some strange intermediate co hair!). For this reason, it is imp length of contact time. Unwa underprocessing than from ove

The complex chemistry and development of specific shades i rules covering certain combina exist. Yellow, orange and red sha already referred to in section : oxidative dyes with other types hair to a lighter shade than the excess to ensure complete and c simultaneously bleach the hair. the bleaching effect. Permanen differences in colour between ir grey hair, which consists of mixe to colour evenly by any other i

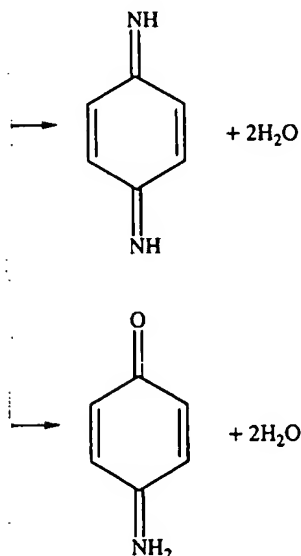
A high pH is necessary and buffered. If significant lighten hydroxyamines such as TEA ca with the semi-permanent dyes, swelling and dye penetration. shampoo-in bases with good we of surfactants (often in conjunct distribution and are most pop

Some of the dye intermediat alkaline solution, even by the ai agents such as sulphites, bisulp to the base. Batches of these pr nitrogen. Opaque or brown gla batch-to-batch colour variation

s are gradually oxidised and then modifiers. The primary intermediates, to a degree, penetrate the hair shaft, and conditions prevailing during the dyeing and coupling reactions produce much of the dye 'trapped' within the hair shaft. The primary intermediate should be devoid of electron-donating groups in the para position. The combinations are either two amino groups, attached to a benzene or heterocyclic ring, or one amino group, either on the ring or on a non-benzene derived (e.g. pyridine).



quinonimine, e.g.



Coupling agents require the substituting groups to be in the 1, 3 positions. They are not easily directly oxidised, but will undergo oxidative coupling with the quinonimines formed from the primary intermediates.

Coupling agents may be based on benzene rings, (substituted or otherwise), multiple ring systems, (fused or unfused), or heterocyclic rings. More than one stage of oxidative coupling may occur, sometimes leading to some very large molecules [118]. The possible reactions, even starting from a blend of relatively few primary intermediates and coupling agents, are numerous. The hair itself may modify or even take part in some of the reactions. The original theory that Bandrowski's bases were intermediates in the dyeing of hair with oxidation dyes is now widely discounted. As well as reaction within the hair shaft, oxidation and coupling simultaneously take place in the solution outside the hair. The multitude of reactions and reaction rates may give rise to some strange intermediate colours in the solution (and sometimes on the hair!). For this reason, it is important to determine and stick to, the correct length of contact time. Unwanted shades are more likely to arise from underprocessing than from overprocessing.

The complex chemistry and reaction kinetics involved mean that the development of specific shades is to a large extent empirical, although general rules covering certain combinations of primary intermediate and modifier exist. Yellow, orange and red shades can be obtained with the nitro derivatives already referred to in section 2.14.2; otherwise it is quite unusual to mix oxidative dyes with other types. Permanent dye systems are able to colour hair to a lighter shade than the original. Peroxide and ammonia, present in excess to ensure complete and controlled oxidation of the dye intermediates, simultaneously bleach the hair. A further increase in the peroxide emphasises the bleaching effect. Permanent dyes are also capable of 'evening-out' the differences in colour between individual hairs. This is especially effective on grey hair, which consists of mixed coloured and white hairs, and is impossible to colour evenly by any other means.

A high pH is necessary and is usually achieved with ammonia, often buffered. If significant lightening is not required (i.e. for dark shades), hydroxyamines such as TEA can be used, and the pH kept a little lower. As with the semi-permanent dyes, solvents are sometimes used to increase hair swelling and dye penetration. Some cream products are available but shampoo-in bases with good wetting properties, obtained using a wide variety of surfactants (often in conjunction with ammonium oleate), ensure even dye distribution and are most popular.

Some of the dye intermediates and modifiers are very readily oxidised in alkaline solution, even by the air and, for this reason, water-soluble reducing agents such as sulphites, bisulphites, dithionites or ascorbic acid are added to the base. Batches of these products are often prepared under a blanket of nitrogen. Opaque or brown glass packaging helps to disguise the inevitable batch-to-batch colour variation of the dye solution.

Permanent colourants cause some hair damage; an increase of alkaline solubility from 6% (natural hair) to 10% (after five applications of oxidative dye) has been reported [119] but is really quite minor. The incorporation of conditioning agents into the base, and the use of post-dyeing shampoos and conditioners allows very good aesthetic effects; leaving the hair not only coloured (lighter or darker) but glossy and with good handle. Oxidative dyes are able to smooth out unevenness in natural hair colour, although caution should be exercised since extra porosity is conferred by bleaching or permanent waving. Hair should not be dyed until several weeks after perming or bleaching.

In developing a range of shades, testing should be carried out on various different hair types, both bleached and unbleached. A variety of colours of human hair tresses can be purchased for this purpose. Initial screening may be carried out on wool, which has a structure closely akin to hair, but final colour tests need to be carried out on real hair. Perceived colour will vary according to the hair type, style, gloss, etc. and also between different ethnic groups [120]. Evaluation is usually carried out by eye, preferably in a light cabinet fitted with 'north daylight' fluorescent tubes to provide standardised viewing conditions. Instrumental colour measurement may also be used [121].

The range of possible intermediates and modifiers is numerous and constantly changing. Some materials once used are now banned, while others are restricted. In the UK, the most up-to-date legislation covering this is The Cosmetic Products (Safety) Regulations 1989, S.I. No. 2233 (1989) and the Cosmetic Products (Safety) (Amendment) Regulations 1993. These are the latest enactments of the EC Cosmetics Directive and include Schedule 1 (materials not permitted) and Schedule 2 (restricted substances). Currently the total concentration of most of the dye intermediates is restricted both individually and in combination. In the USA, the use of colours in cosmetics is controlled by the FDA. Phenylene diamines, diamino phenols, α -naphthol, pyrogallol and resorcinol are all, for instance, restricted. Oxidation hair dyes are also required to carry a warning since many of the intermediates and modifiers are allergens and sensitisers. The warning must appear in the

statutory form as prescribed by the regulations. This has generated a huge number of patents and has made the decision when deciding a formula.

Table 2.35 gives typical formulations for oxidation hair-dye bases. In formulation B the salt level must be adjusted on dilution with an equal volume of water. The dye intermediates themselves can be used in various proportions and base may need to be varied for different shades.

2.14.4 Other hair dyes

Some hair colourants do not fall into the permanent/permanent classification based on henna [122]. The dried leaves of henna are ground and applied as a paste to the hair. The paste is left on the hair for several hours, such as indigo or camomile. (Indigo is not added.) A less satisfactory alternative is the use of an extract of henna leaves as a base. This has a number of disadvantages—the limited range of colours (when using henna alone), but the use of henna alone gives unnatural colours), a long contact time, and the need to heat the hair to obtain the best effect. A less satisfactory alternative is the use of 2-hydroxy-1,4-naphthoquinone, which has a good record of non-irritation and is mildly acid.

Most women, when faced with the choice of grey hair, opt for grey of their choice. Most men in the same situation opt for grey. These products are based on lead-sulphur dye. These products precipitated sulphur, both at 1–2% and 5–10% amounts of a wetting agent, but the products are applied regularly and the hair is washed, leading to a gradual loss of colour. This is not always very natural looking. The exact mechanism of the reaction is not known and should be handled with care.

2.14.5 Dye removers

No dye removers are completely effective. They are of a temporary nature, will eventually wash out, and the hair will fade slightly as they 'grow out'. They are obtained with sulphites and sodium formaldehyde sulfoxide to improve the effectiveness of such

Table 2.35 Formulations for oxidation hair-dye bases

	A	B
Isopropanol	7.5	—
PPG-2 methyl ether	—	1.8
Oleic acid	22	4
Coconut diethanolamide	10	11
Sodium lauryl ether sulphate, 27%	—	36
Salt	—	q.s.
Deionised water	to 100	to 100
Ammonium, 0.880	6.6	2

damage; an increase of alkaline after five applications of oxidative is quite minor. The incorporation of the use of post-dyeing shampoos has little effect; leaving the hair not only with good handle. Oxidative dyes restore natural hair colour, although caution is conferred by bleaching or until several weeks after perming.

should be carried out on various bleached. A variety of colours of is purpose. Initial screening may be are closely akin to hair, but final al hair. Perceived colour will vary and also between different ethnic id out by eye, preferably in a light cent tubes to provide standardised measurement may also be used

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statutory form as prescribed by the Regulations. Hair dye intermediates have generated a huge number of patents and due regard must be paid to these when deciding a formula.

Table 2.35 gives typical formulations for oxidation hair-dye bases. In formulation B the salt level must to be adjusted to give the required viscosity on dilution with an equal volume of hydrogen peroxide solution. The dye intermediates themselves can have a considerable impact on the viscosity, and base may need to be varied from shade to shade to compensate for this.

2.14.4 Other hair dyes

Some hair colourants do not fall neatly into the temporary/semi-permanent/permanent classification. These include the vegetable dyes, mostly based on henna [122]. The dried leaves of the henna plant are powdered and applied as a paste to the hair, either alone or mixed with other plants such as indigo or camomile. (Diluents, fillers, thickeners, etc. can also be added.) A less satisfactory alternative is the preparation and use of an aqueous extract of henna leaves as a base. The use of henna as a hair dye has a number of disadvantages—the limited range of shades attainable (all reddish when using henna alone), build-up on repeated use (leading to rather unnatural colours), a long contact time, and the need to apply the product hot to obtain the best effect. Advantages are that the product is 'natural' and has a good record of non-irritancy. The main active ingredient is lawsone (2-hydroxy-1,4-naphthaquinone), also present in walnuts. The optimum pH is mildly acid.

Most women, when faced with greying hair, will simply dye it to the colour of their choice. Most men in the same situation will either persuade themselves that greying hair looks distinguished or assuage their vanity by using a lead-sulphur dye. These products consist of a solution of lead acetate and precipitated sulphur, both at 1–1.5% in an aqueous base, usually with a small amount of a wetting agent, humectant, and sometimes a little solvent. The products are applied regularly and left on the hair, where a slow reaction takes place, leading to a gradual build-up of a brownish colour. The effect is not always very natural looking and the hair may be left a little dull. The exact mechanism of the reactions is not clear. The products are toxic and should be handled with care.

2.14.5 Dye removers

No dye removers are completely successful. Semi-permanents, by their very nature, will eventually wash out, whereas permanent dyes will usually only fade slightly as they 'grow out' naturally. A limited degree of success may be obtained with sulphites and other related reducing agents, in particular sodium formaldehyde sulfoxylate. The use of activated charcoal can improve the effectiveness of such bases but is unsightly and messy [117].

Table 2.35 Oxidation hair-dye bases

A	B
7.5	—
—	1.8
22	4
10	11
—	36
—	q.s.
to 100	to 100
6.6	2